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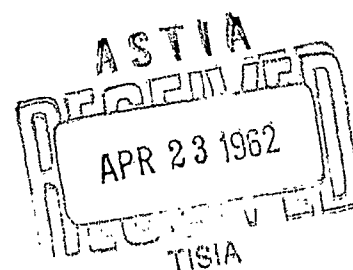
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Technical Report

R 190

INFRARED MEASUREMENT OF
SULFONATE ADDITIVES

11 April 1962



U. S. NAVAL CIVIL ENGINEERING LABORATORY

Port Hueneme, California

INFRARED MEASUREMENT OF SULFONATE ADDITIVES

Y-R011-01-014

Type C Final Report

by

J. B. Crilly, R. J. McGowan

OBJECT OF TASK

To develop a lot acceptance test for preservative lubricants and to develop reliable techniques to readily identify preservative additives.

ABSTRACT

Infrared spectra of 18 oil samples, to which varying concentrations of sulfonate were added, were made and plotted on graphs. It was shown that there was a correlation between concentration and absorption of the sulfonate inhibitors. The method is based on the fact that sulfonates absorb at wave lengths between 9 and 10 microns when exposed to infrared radiation. This absorption was found to be directly proportional to the concentration of the sulfonates and so may be used to measure content of sulfonates in oils.

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INTRODUCTION

The application of infrared spectrometry to chemical problems began in 1900 with the exploratory work of Coblentz.¹ In about 1935, this equipment began to be used in industrial laboratories to identify unknown materials by spectral matching with known substances.² The use of infrared spectroscopy as a research and analytical tool has increased in recent years, because it gives more detailed information and saves a great deal of time compared with other methods.

It is an excellent means for determining the composition of organic compounds in terms of molecular structure. All organic and most inorganic compounds have unique infrared spectra that make it possible to determine their presence in chemical structures. The application of this technique to the detection of sulfonate additives used in petroleum products is only one of the many uses of infrared spectroscopy.

The electromagnetic energy emitted by any warm body is known as infrared radiation. This differs from visible light only in being of a lower frequency. The absorption and transmission of this radiation depends on many factors, the principal one being the chemical structure of the substance examined. When the frequency of this infrared radiation is equal to a characteristic vibration frequency of the molecule through which it passes, it is absorbed.

When a sample is placed in an infrared spectrophotometer, infrared radiation of varying frequency (625 to 4000×10^{12} cycles per second) is passed through the sample. At any point in this range where the frequency of the radiation is equal to a characteristic frequency of the sample, absorption occurs and is recorded on a chart.

The method described in this report is based on the fact that the sulfonates absorb in the wave-length region between 9 and 10 microns. Results show that this absorption is directly proportional to the concentration. Therefore, infrared techniques offer a rapid and accurate method for determining the concentration of sulfonates.

The preservation of an internal combustion engine is essential in the storage of automotive equipment, and this can only be done by covering the parts of the engine with a protective coating. The suggestion has been made that maintaining a separate stock of preservative lubricants could be avoided by simply adding a preservative to the oil already in an engine just before it was to be placed in storage. Villanova University is working, under a Bureau of Yards and Docks contract, on the evaluation of different types of preservative additives for use in the storage of automotive equipment. Oil films had been inadequate for this purpose until it was found that their preservative quality could be greatly increased by the addition of organic polar compounds such as the sulfonates. Since moisture must be present for corrosion to occur, keeping the surface free of moisture will prevent corrosion. The function of sulfonates in oil is to keep the oil on the surface of the engine parts, in order to prevent moisture coming in contact with them.

These polar compounds are not corrosion preventives in themselves, but, when added to a lubricating oil, they increase its capacity to inhibit corrosion. Because they are polar compounds, the sulfonates form a lattice film, containing oil, over the surface of the metal, keeping moisture from the metal surface.³

An important factor in the formation of this rust-preventive film is the concentration of the sulfonate in the oil. It is usually between 1 and 4 percent. The sulfonate concentration can be determined by "wet" chemical methods, which require 8 hours; but, with infrared spectroscopy, the analysis can be made in minutes.

PREPARATION OF SAMPLES

In order to study the absorption of sulfonates in oil, samples of oils containing varying amounts of sulfonates were prepared. Barium dinonyl naphthalene sulfonate (a 50-percent solution in light mineral oil) was used.

Ten samples, with sulfonate concentrations ranging from 1 to 4 percent by weight in oil (which conformed to Military Specification Mil-L-9000E), were heated and mixed on a magnetic stir-plate at 90 C for one hour. The samples were then cooled to room temperature, placed in a sample cell of 0.09-millimeter nominal thickness, and examined on a Beckman IR-5 Infrared Spectrophotometer. The complete instrument spectrum is from 2 to 16 microns, but, in these studies, only the 8- to 11-micron portion of the spectrum was used to show the sulfonate absorption and background. Preparation of each spectrum required only 5 minutes.

DATA

The calculations are based on the fact that concentration is proportional to absorption.

$$C = kA$$

where C = the concentration per 100 grams of solution

k = the extinction coefficient characteristic of the material and the wave length

$$A = \log_{10} \frac{T_B}{T_P}$$

where T_B = the background transmission

T_P = transmission at the peak

T_B is obtained by drawing a straight line tangent to the spectrum curve at the position of the absorption band to be determined (Figure 1). T_P is the transmitted radiation and is measured at the point of maximum absorption (Figure 1), with an NaCl window in the reference beam. Figures 2 and 3 show the effect of putting a cell containing untreated oil in the reference beam to compensate for background absorption and reflection losses.

$k = C/A$ is, for this instrument and this analysis, equal to 16.67. It is the slope of the line relating absorption and concentration in Figures 3 and 4. By comparing these figures, it can be seen that the effect of using compensation in the reference beam is to shift the intercept of the line and to change the slope. The line, however, now shows zero absorption at zero concentration. In the absence of standards, the concentration can be approximated by the following:

$$C = 16.7 (A - 0.14) \text{ without compensation}$$

$$C = 38.5A \text{ with compensation}$$

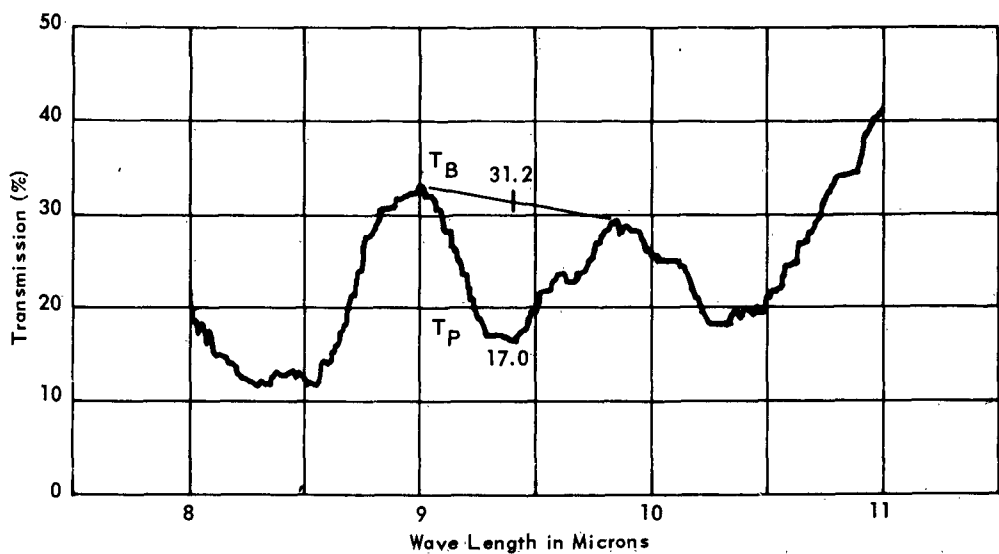


Figure 1. One-percent solution of barium dinonyl naphthalene sulfonate in oil, not compensated by oil in the reference beam.

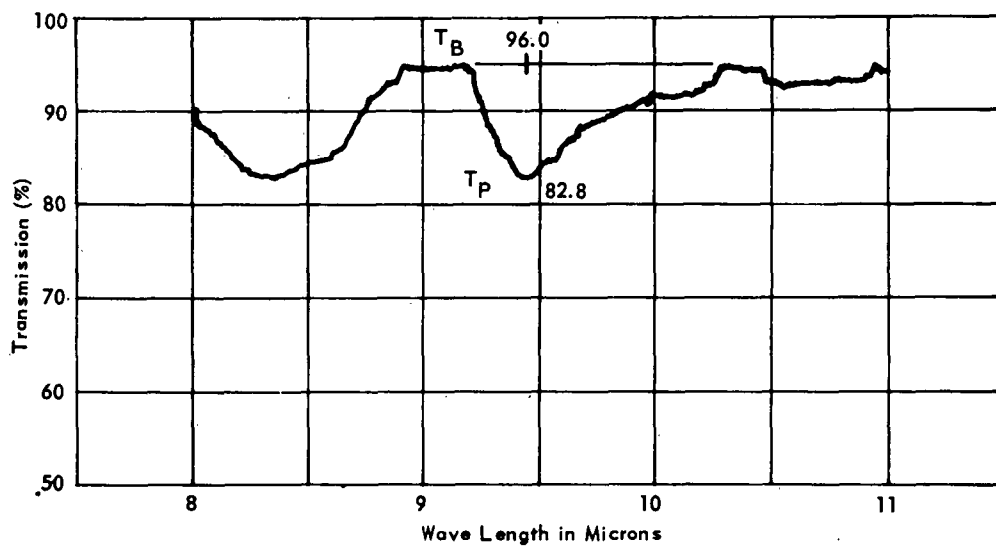


Figure 2. One-percent solution of barium dinonyl naphthalene sulfonate in oil, compensated by oil in the reference beam.

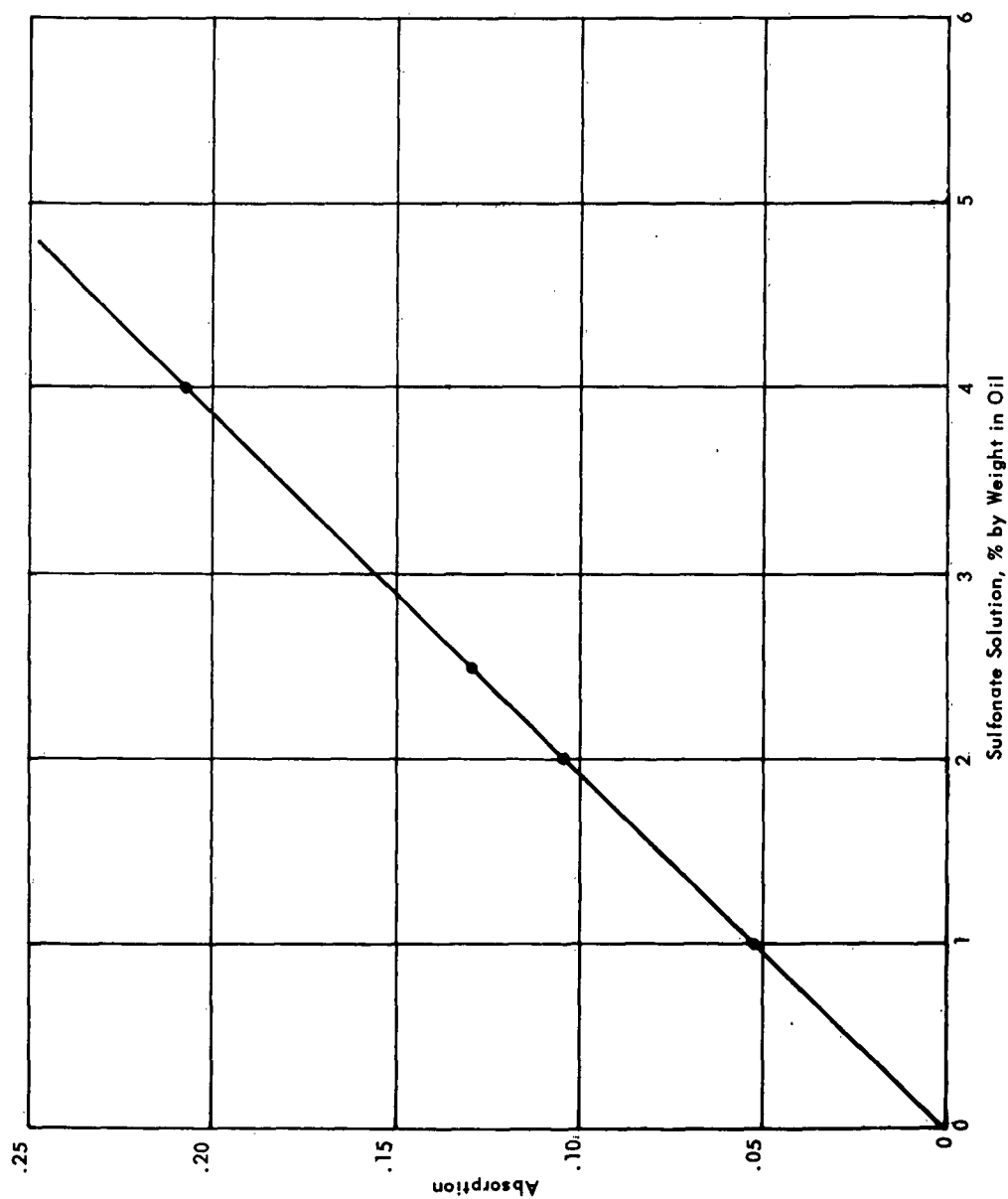


Figure 3. Absorption of barium dinonyl naphthalene sulfonate solution in oil (Mil-L-9000E, type 9250), compensated by oil in the reference beam.

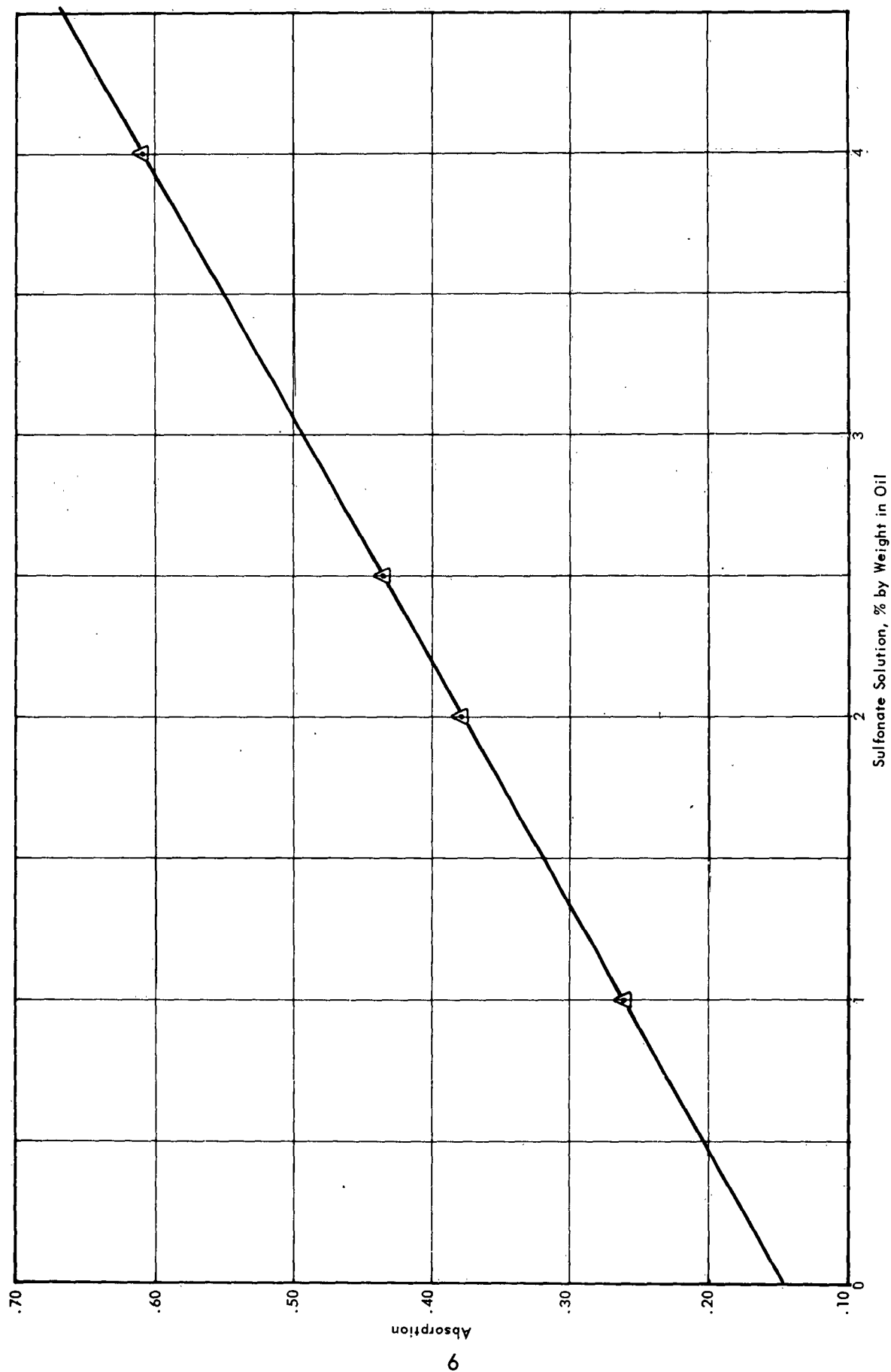


Figure 4. Absorption of barium dinonyl naphthalene sulfonate in oil, (Mil-L-9000E, type 9250), not compensated by oil in reference beam.

The following tabulation shows some of the data from Figure 4:

Concentration of Sulfonate % by Weight (NaCl in reference beam)	T_B	T_P	$\frac{T_B}{T_P}$	A
1.00	31.2	17.0	1.835	.26
2.02	30.3	12.5	2.424	.38
2.52	30.4	11.0	2.764	.44
4.06	27.0	6.5	4.154	.62

The following tabulation shows the data from Figure 2:

Concentration of Sulfonate % by Weight (oil in reference beam)	T_B	T_P	$\frac{T_B}{T_P}$	A
1.00	96	83.0	1.132	.05385
2.02	92	72.5	1.269	.10346
2.52	96	71.5	1.345	.12872
4.06	91	56.5	1.613	.20763

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1. Carnegie Institution. Publication No. 35, Investigation of Infra-Red Spectra, by W. W. Coblentz. Washington, D. C., 1905.
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FINDING

The concentration of barium dinonyl naphthalene sulfonate in oil is directly proportional to its absorption.

CONCLUSIONS

1. The use of infrared spectrophotometry is feasible in measuring sulfonate additives in preservative oils.
2. The infrared technique is a much more rapid means of analysis than "wet" chemical method.
3. The infrared technique is the most economical method available.

RECOMMENDATION

If sulfonates are added to crank case oil when an engine is put in storage, periodic analyses should be made to insure the continued proper concentration.

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